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The Role of Fiber Mechanical Treatment on the Retention of Cationic Starch

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Mechanical Treatment on the Retention
of Cationic Starch

by

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ABSTRACT

Cationic starches possess a positive or cationic charge. Because of this charge, they have found widespread use at the wet end of the papermachines. When applied properly, cationic starches have been found to increase filler and fines retention, improve interfiber bonding, increase pick resistance and reduce BOD in mill effluent. In order to obtain these benefits, it is first important to retain the cationic starch in the sheet.

Several factors have been determined to affect cationic starch retention. These factors include - pH, starch molecular weight, starch charge density, rate of application, retention aid used, furnish type and degree of fiber mechanical treatment. It was discovered that a discrepancy existed in the the role of fiber mechanical treatment on the retention of cationic starch. An experiment was designed and conducted to charify what effects fiber mechanical treatment had on the retention of cationic starch under conditions that simulate the wet end of a papermachine.

It was found that as fiber mechanical treatment was increased, the retention of cationic starch increased to a maximum, then decreased as a greater amount of fines was lost in the white water.

It was also found that in the absence of fines, fibers themselves retained more cationic starch because they were subjected to mechanical treatment.

OBJECTIVES

The objective of this work is to experimentally determine the relationships that exist between fiber mechanical treatment and the retention of cationic starch.

Key words:

Starch

Cationic

Absorption

Mechanical treatment

Retention

Fines

Surface area

Charge

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INTRODUCTION

Many topics are discussed in the following literature review which required investigation in order to form a sound basis for research. Topics such as starch, cationic starch, attributes of cationic starch and retention of cationic starch are discussed. A statement of a problem and justification for research are included as well as an experimental design. The reaults obtained through the experiment are presented and discussed. Conclusions are made which show a relationship between fiber mechanical treatment and cationic starch retention.

HISTORY AND DEVELOPMENT OF STARCHES

STARCH SOURCES AND GRANULE APPREARANCE

Wurzburg (21) states that starch is a white granular substance that occurs widely in nature. These granules are mainly deposited in the seeds, tubers, or roots of plants.

While starch occurs throughout the plant world, there are only a limited number of plants which are utilized for the production of commercial starch. Maize is the major source of most starch produced. Starch found here is extracted from the seeds or kernels. Other sources of commercial starch are potatoes and tapioca. These sources contain starch in the roots or tubers. Wheat, rice and sago are also sources of commercial starch.

It is common knowledge that starch granules are insoluble in cold water. Wurzburg (21) also stated that the granules vary in size and shape depending on the plant source. He described rice granules as being polygonal in shape and between 3 and 8 m in diameter in clusters. Corn starch is described as being polygonal and/or round and ranging from 5 to 25 m. Potato starch has the largest granules of any commercial starch. The granules are oval or egg-shaped and range from 15 to 100 um.

According to Watson (2) various types of processes are used in the manufacture of starch, depending upon the plant source. In general, they involve freeing starch granules from the other constituents such as the fiber, germ protein and extraneous materials; purifying it, usually by screening, washing and utilization of centrifugal separators; and then dewatering and drying. With corn starch, the mechanical separation is made easier by steeping the grain in warm water in the presence of sulfite. Normally the manufacture is carried out in aqueous suspensions since, as previously stated, starch granules are insoluble in water at relatively low temperatures.

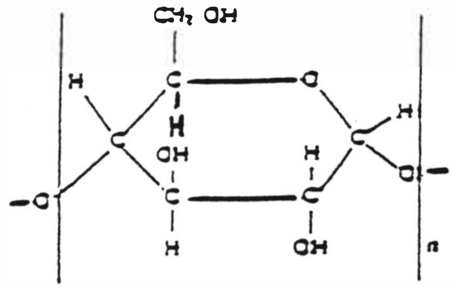
STARCHES IN PAPERMAKING

Starch has been beneficial to papermaking for many years. Until the 1950's its use at the wet end was limited to increasing strength properties where nonderivatized "Pearl Starches" were used (15). The development of starch modifications has widened its use immensely. Where starch was once used only as a wet end additive to improve dry strength it now finds use to improve fines and filler retention, surface sizing, pigmented coating, and converting adhesive functions (17). The scope of this paper will limit discussion to the wet-end applications, moreover, to the retention of cationic starches.

CATIONIC STARCHES

CHEMISTRY AND STRUCTURE

Starch is a polysaccharide in which the basic repeating unit is an anhydroglucose unit as shown below (6).



ANHYDRO GLUCOSE UNIT

In nature, starches occur as a mixture of linear and branched molecules. The linear fraction is called amylose. The branched fraction is called amylopectin. Harvey (6) states that the ratio of amylose to amylopectin varies depending on the starch source. Variations in ratio of amylose to amylopectin result in variations in the viscosity, molecular weight, and charge distribution of cationic starches.

Solarek (16) explains that cationic starches are produced by a chemical reaction of starch with reagents containing amino, imino, ammonium, sulfonium, or phosphonium groups, all of which can carry a positive charge. Currently the commercially significant derivatives are the tertiary amino and quaternary ammonium starch ethers. The key factor in their usefulness is an affinity for negatively charged substrates. In papermaking, the cellulosic fiber and fines is this primary substrate, and cationic starches have found large-scale use in the paper industry as wet-end additives (5).

Roberts (13) explains that tertiary and quaternary cationic starches are less sensitive (charge more stable) to pH than are primary or secondary cationic groupings. Harvey, et.al (6) reinforces what Roberts suggested by stating that as the cationic grouping progresses from primary to secondary, to tertiary, to quarternary, the charge intensity is increased. Also, as the cationic grouping progresses from primary to quaternary, the sensitivity to pH changes is decreased.

A common reagent use for the preparation of a tertiary amine cationic starch is diethylaminoethyl-chloride hydrochloride:

$$(C_2H_5)_2\text{-}NCH_2\text{-}CH_2\text{-}Cl - HCl$$

when reacted with starch, the product obtained is:

$$\text{Starch} - R - O - C_2\,H_4\,N\,(C_2\,H_5)_2\;\;HCl$$

Likewise, a typical reagent used for the preparation of cationic starch with a quaternary group is epoxypropyltrimethylammonium chloride.

$$CH_2 \overset{O}{\frown} CH - CH_2 - N^+(CH_3)_3 + Cl$$

The resulting cationic starch may be shown as:

$$\text{Starch} - R - O - CH_2 - CHOH - CH_2 - N^+ - (CH_3)_3 + Cl^-$$

Cationic starches are usually purchased precationized from the starch producer (13). Cationic starches are traditionally prepared in a granular state as follows (6):

A starch slurry is dispersed in water at a desired concentration. Salts such as sodium chloride or sodium sulfate are added to prevent swelling or gelatinization of the granules during the reaction. Alkali such as sodium hydroxide is added to promote the reaction. The selected cationic reagent is added and the reaction is usually carried out for 12 to 20 hours at about 110°F.

The reaction product is then washed and filtered to remove the salt and unreacted reagent. dried and packaged.

On-site reactions can be conducted with starch being in the granular state, however, to eliminated difficulties associated with granular reaction such as long reaction time, swelling inhibitors, and washing reactions are usually conducted in a pasted state. This method has met some success according to Harvey et. al.(6).

Retention of Cationic Starches

It has been known for a long time that wet end starch imnproves dry strength, especially inter fiber bonding in the sheet (7,10, 12, 13, 14).
Liinstrom (9), also suggtests that these polysaccharids act as lubricants between the fiber surfaces in the wet state, minimizing the intensity of local stress concentrations in the sheet.

Experience gathered in many mills confirms that cationic starch improves interfiber bonding, increases pick resistance, and under certain conditions, improves drainage and increases fines retention. Cationic starcheshave also been reported to improve sheet formation, increase sizing efficiency, wet strength, and reduce BOD as compared to regular (slightly anionic) starch which is less well retained (7, 10, 12).

In order to assure the economic and stsrength advantages sought for the sheet, and to lessen waste disposal concerns (high BOD) caused by unretained stqwarch, efficient absorption of the starch on the fiber is imperative.

Harvey (7) states that several factors can affect cationic starch retention.

These factors include degree of substitution, type of furnish, rate of applicaton, method of addition and use of retention aids.

Marton and Marton (10) also suggest that molecular weight has some influence on the performance of starches, as well as fiber source, charge density and degree of fiber treatment. Both Moeller (12) and Roberts et. al.(14) are in agreement with the aforementioned but tend to stress pH and degree of fiber treatment.

Degree of Substitution

The extent of cationization in commercial cationic strarches is approximately equivalent to a degree of substitution of 0.02. That is for every 100 glucose units, on average, there are two cationic groups.

Marton and Marton (10) surmised that the higher the charge density (D.S.) the more it affects formation and retention of fines. Also, if excessive starch is used, the cationic charge may be overdosed resulting in redispersion of the fines by charge reversal and overflocculating the fiber.

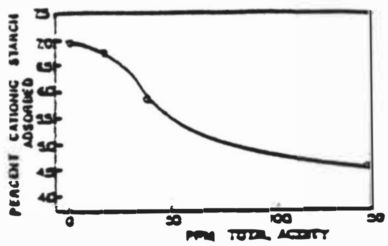
The work of Harvey (7) was in agreement with what Marton had surmised. Harvey stated, however, that cationic starches of low degree of substitution D.S.) exhibit shear sensitivity. He went on to say that retention of cationic starches appears to stabilize with increasing D.S. Also adding that the effect of the starch on the surroundings (furnish) must also be a factor in starch retention.

Molecular Weight

Cushing and Schuman (3) found in their work with pearl starches that as the molecular size decreased the starch retention decreased. Marton and Marton (10 later found in their work with cationic starches that molecular weight did have some influence on the performance of starches. They stated one obvious effect was on the viscosity of the starch solution. As the molecular weight of the starch was increased, the diffusion rate of the starch molecules and therefore the rate of absorption was decreased. The higher moleclar weight starches did show more shear resistance which would possibly increase their retention under higher shear conditions.

pH

The work of Moeller (12) showed that as total acidity increased the percent of cationic starch absorbed decreased. His results are shown in Figure 1.



○ 700 ml CSF □ [illegible] ml CSF △ 510 ml CSF ● 420 ml CSF ■ [illegible] ml CSF

Fig. 1 [illegible] of [illegible] in [illegible] on [illegible] cationic starch adsorption by [illegible] [illegible] pulp at 410 ml CSF

The work of Roberts et. al. (14) confirmed the results of Moeller. Roberts stated that the effect of pH is predictable. It is known that the negative surface charge exhibited by cellulose fibers results from the dissociation of uronic and saccharinic acid groups as shown by Marton (11). "This charge decreases with a decreasing pH as a result of protonation of the carboxyl groups (Figure 2)".

This explains the low affinity for cationic starch at low pH. Native starch, having no cationic groupings, would not be expected to show this effect.

Fig. 2. The effect of pH on the surface charge of cellulose.

$$\text{cellulose} - COOH \xrightleftharpoons[\text{low pH}]{} \text{cellulose} - COO^{\ominus} + H^{\oplus}$$

Fiber Mechanical Treatment

The work of Moeller (12) showed that absorption of starch, both pearl and cationic, increased with increased refining (Fig 3.) Marton and Marton (10) also found that cellulosic fines ($<$200 mesh) retain more cationic starch than fibers do. It is well known that fines have a larger surface area than fibers. Refining also increases the surface area of the fibers, thus explaining the work of Moeller. Marton and Marton (10) also stated that retention of cationic starch varies with various fiber sources. They showed that pine and hardwood kraft fibers can retain roughly the same amount of cationic starch. Also, that dried pulps retain less than never-dried pulps, and unrefined pulps less than refined. They explained this by saying that drying reduces the swellability of the fibers upon rewetting. Swelling can create higher surface areas, and can expose more active sites on the surface available for starch absorption. Potentially reactive bonding sites are fewer as a result of drying in an irreversible way.

Roberts et. al.(14) results were in complete contradiction with the work of others on this subject (Figure 4). He believed a more accurate method to determine starch retention was by labeling the starch with C^{14} and measuring the retention via liquid scintillation counting. Roberts stated that refining reduced the retention of cationic starch but increased that of native starch. The effect of cationic starch has been explained by Marton (11) through the loss of fines at high levels of refining. Roberts stated, however, that this explanation was not acceptable. He went on to explain that the retention of cationic starch by fibers that had been fractionated on a 24-mesh screen for 10 minutes showed little difference from unfractionated fibers (Table 1). Furthermore, by continuously recycling stock through a handsheet machine (using fresh water each time), the retention fell only slightly and exhibited the same slope for beaten as for unbeaten fibers (Figure 5). Both of these results, stated Roberts, suggest that cationic starch has an inherently lower affinity for refined fibers than for unrefined fibers.

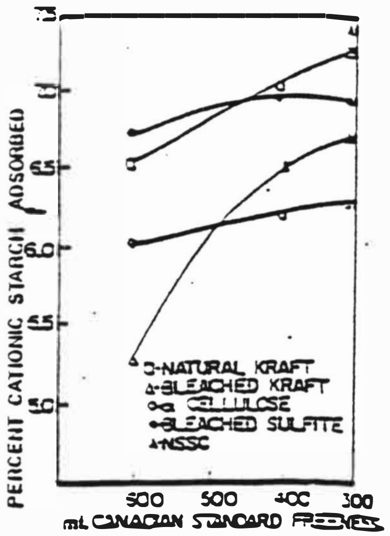


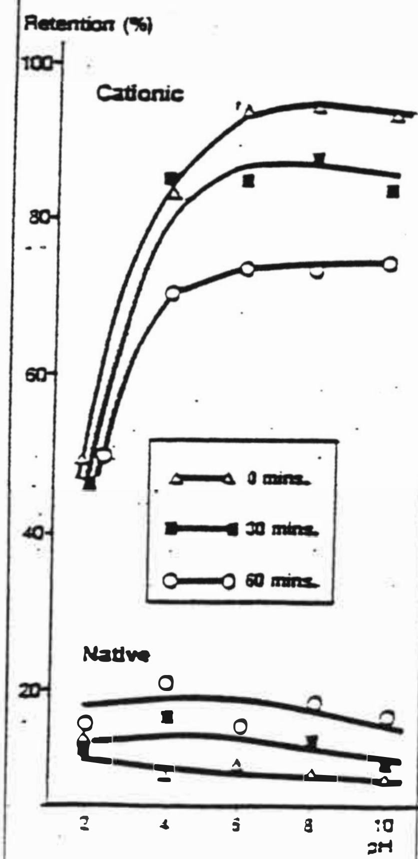
Fig. 3 Maximum cationic starch adsorbed by five pulps at various CSF levels

Table 2 Retention of cationic starch

	Unbeaten	Beaten
Before, %	71.8	58.0
After, %	71.3	61.1

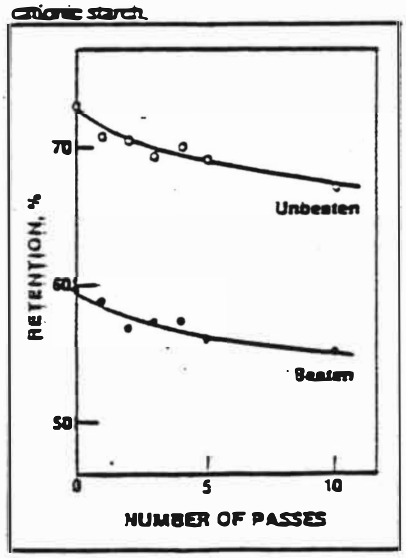
10 min, 24-mesh screen, bleached softwood sulfate pulp.

FIGURE 4 EFFECT OF BEATING AND pH ON RETENTION OF NATIVE AND CATIONIC STARCH*



*For a bleached softwood sulfate pulp.

5 The effect of successive passes through a handsheet machine on the retention of cationic starch.



STATEMENT OF PROBLEM

A literature survey has been presented discussing the background, chemistry, attributes and importance of retention of cationic starches in a sheet of paper. Variables affecting starch retention were also included.

Upon review of the literature and previous experiments, it becomes very evident that there exists a knowledge gap pertaining to the effects of fiber mechanical treatment on the retention of cationic starches.

JUSTIFICATION FOR STUDY

By varifying how retention of cationic starch is affected by refining, the economic and strength advantages sought for the sheet may be more easily obtained. Also, waste disposal concerns caused by unretained starch can be minimized.

EXPERIMENTAL APPROACH AND DESIGN

The effect of fiber mechanical treatment on the retention of cationic starch was the objective of this study. In order to do this, it was necessary to control all other variables that have been determined to affect cationic retention. Table II lists these variables and the controlled conditions that were met.

Table II: Controlled Variables and Conditions Met

Variable	Condition
Furnish type	Constant pulp source
pH	8.0- ± 0.2
Molecular Weight	Constant Starch Source
Degree of Substitution	Constant Starch Source
Rate of Application	20 Lb starch/Dry ton Fiber
Retention Aid	None
Method of Application	Added in 1% Solution to stock

The constant pulp source was a Canadian bleached kraft hardwood. The constant starch source was a pregelatinized quaternary cationic potato starch.

The manipulated variable in this experiment was the degree of fiber mechanical treatment. This was done using a laboratory Valley Beater.

Since fines are believed to play an important role in the retention of cationic starch and fibers are believed to have a minimal effect, it was desirable to remove the fines from the furnish. This was done using the Clark Classifier where fines are defined as anything passing through a 100 mesh screen and the fiber portion recovered between the 50 and 100 mesh screens. The two furnishes and refining levels of each are given in Table III.

Table III: Level of Mechanical Treatment

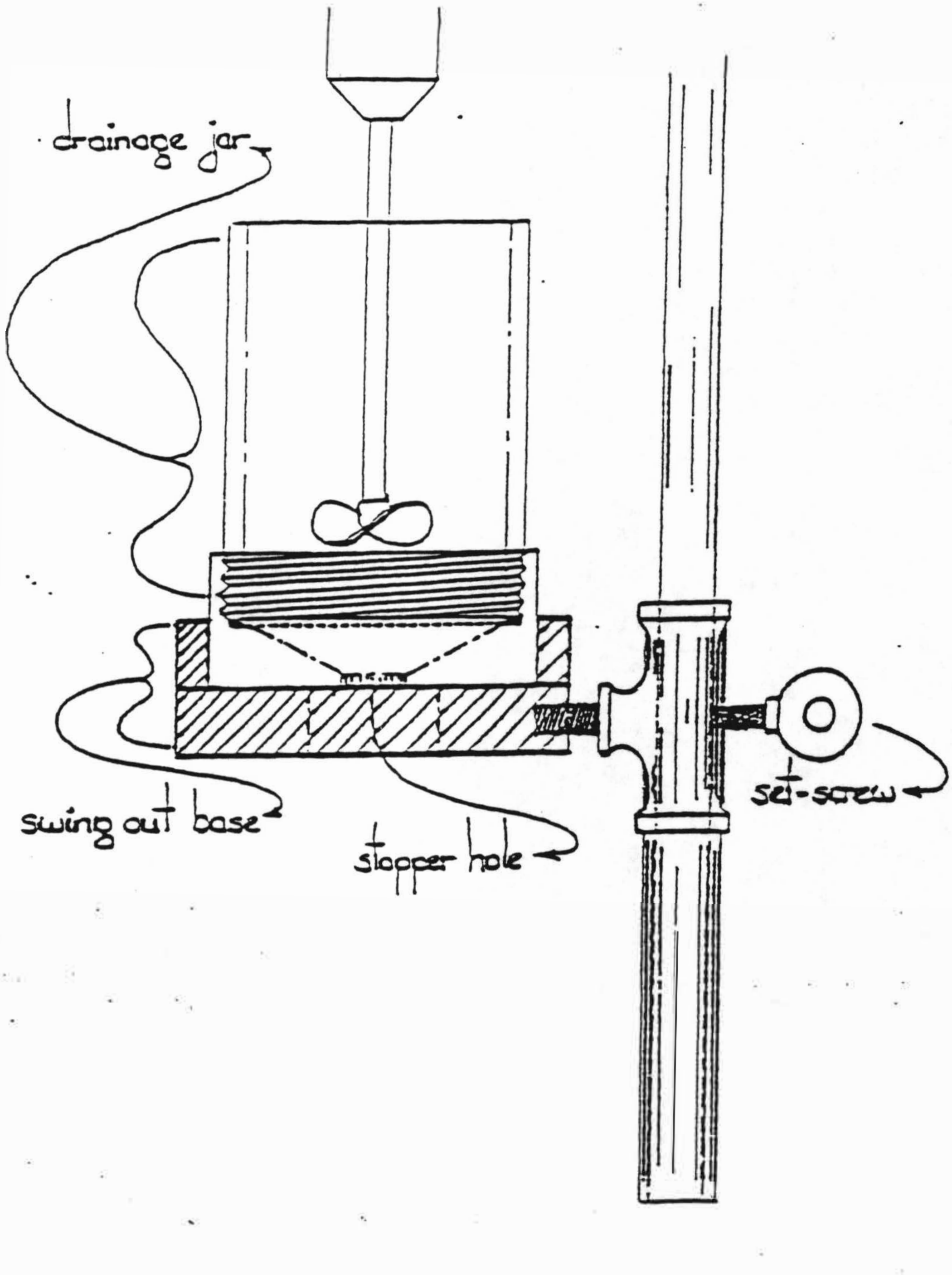
Furnish	Refining Time (min)
1	0
1	20
1	40
1	60
2	0
2	20
2	40
2	60

Furnish one was unclassified, furnish two was the classified pulp.

After the samples were taken from the Valley Beater and classified, as in the case of furnish two, each was formed into a filter pad with a Buchner funnel. Then pulp consistencies were the determined and the furnish pads were sealed in Ziplock bags and stored for later use.

On the papermachine, forming of the sheet takes place under turbulent conditions with strong hydraulic shear tending to carry the fine particles through the web and into the white water. It follows that the commonly used laboratory sheet making devices, where turbulence is low and deliberately avoided, usually fail to predict behavior on a papermachine. The Dynamic Drainage Jar was developed as a means for the study of paper stock in the laboratory under conditions of controlled and graduated turbulence. Since the Dynamic Drainage Jar is the best known way to simulate the wet end of a papermachine in the laboratory, this apparatus was chosen for use in this experiment.

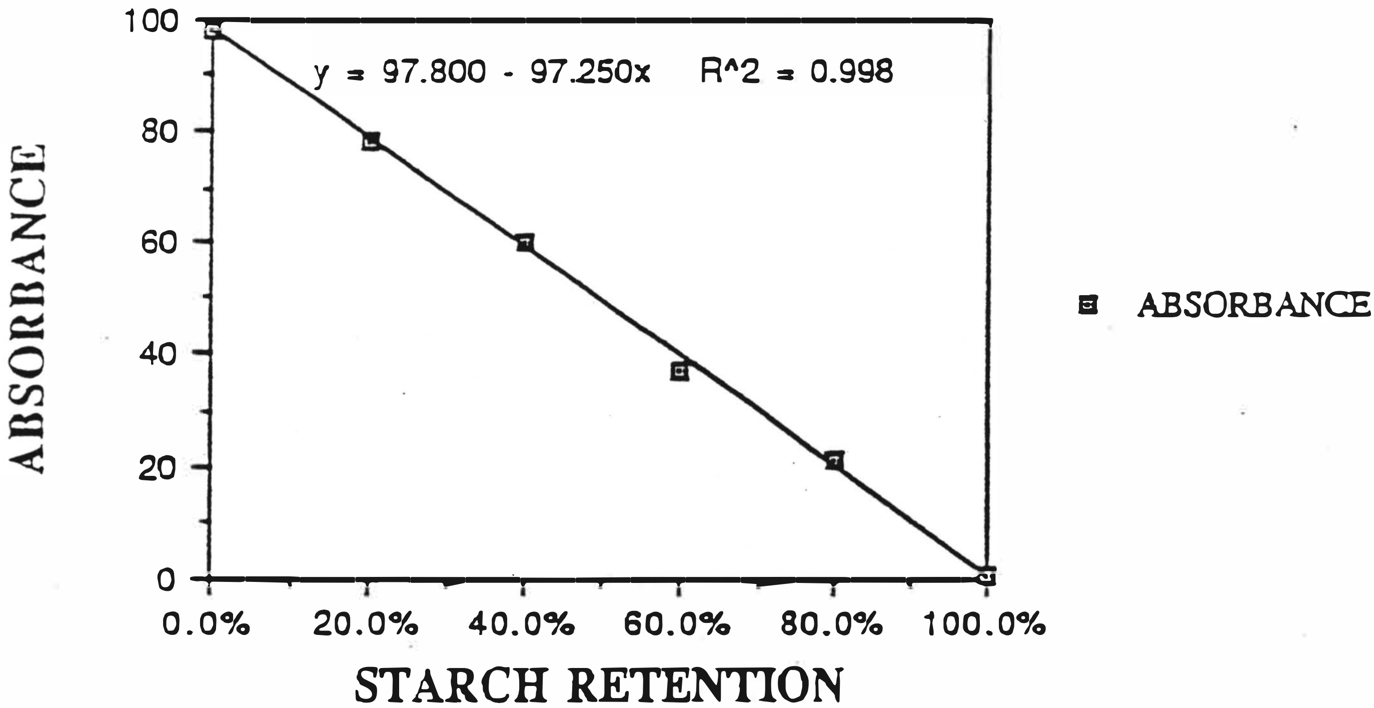
FIGURE 6 : Dynamic Drainage Jar



Four starch determinations were performed at each refining level for both the unclassified and the classified pulp furnishes. The entire process was then repeated a total of three times. This was done to measure the variance of the results.

To convert the spectrophotometer readings into starch retention values, it was necessary to develop a calibration curve. This was done prior to the actual experiments. To develop the calibration curve, the same procedures were followed as for the Drainage Jar filtrate samples. A known amount of starch was present in calibration solutions which could be correlated to the percent retained and plotted against the absorbancy readings from the spectrophotometer. Figure 7 shows the calibration curve that was obtained. An equation relating absorbancy and percent starch retained was developed statistically. This equation made it possible to determine the starch retention directly from an absorbancy reading from the spectrophotometer.

FIGURE 7 STARCH RETENTION VS. ABSORBANCE



PRESENTATION OF RESULTS AND DISCUSSION

The results for this experiment are presented and discussed from two aspects, that of the effects of fiber mechanical treatment on the retention of a cationic starch with a full unclassified furnish, and that of a classified furnish in the absence of fiber fines. References are made to work that has been done in this field of study in order to clarify the contradiction that existed.

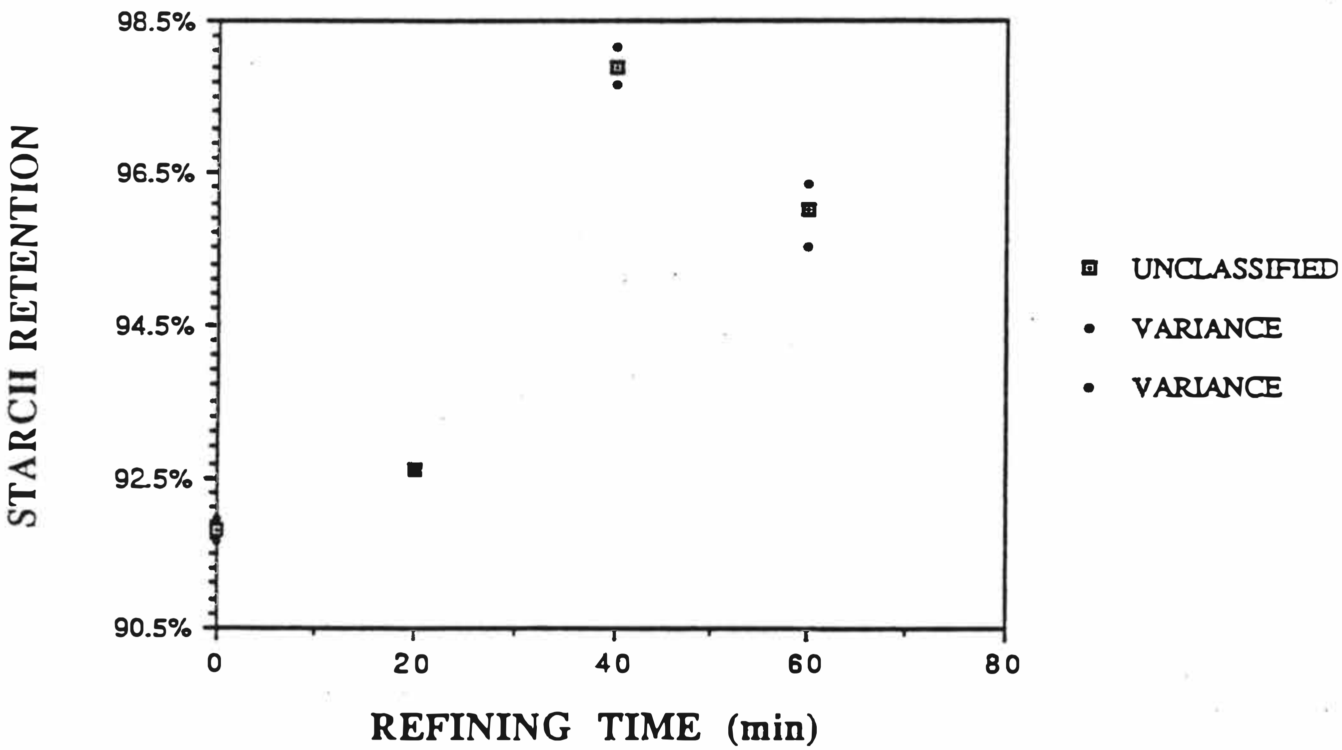
UNCLASSIFIED PULP

The effect of fiber mechanical treatment on the retention of a cationic starch is presented in Figure 8.

It is evident from this graph that as fiber mechanical treatment is increased, the retention of cationic starch also increases. These results show the same trends as those of Moeller (12). An explanation is that as the degree of fiber treatment is increased, a greater number of fines are created. It is well known that fines possess a greater surface area than fibers do. Refining also increases the surface area of fibers and causes them to swell. Swelling can expose more potentially reactive sites on the fiber surface for starch absorption.

This phenomenon also explains the slight decrease in retention at the highest level of refining. At this point there exists such a large amount of fines that it is difficult to retain them in the sheet or Drainage Jar. Since the surface area of the fines is much greater than that of the fibers, they will absorb much more starch. The starch retention then decreased as a result of being carried out with the fines.

FIGURE 8   UNCLASSIFIED PULP
REFINING TIME VS. STARCH RETENTION



CLASSIFIED PULP

Figure 9 shows the effect of fiber mechanical treatment on the retention of a cationic starch in the absence of fiber fines. These results show the same trend as that of a total furnish, fines included - Figure 10. As previously stated, refining creates fines but also increases the surface area of fibers causing them to swell and expose more potentially active sites for starch absorption. In the absence of fines, the starch will absorb onto the fibers since there are no fines to absorb the starch. Roberts et. al. (14) found that classified pulp showed the same trend as unclassified pulp. He found, however, that the retention of cationic starch decreased with an increasing amount of fiber mechanical treatment.

It is difficult to understand why the classified pulp also showed a slight decrease in starch retention at the highest level of fiber mechanical treatment. One would expect, since there were no fines present, that the highest level of fiber mechanical treatment would yield the highest level of starch retention.

During the experiment, however, it was observed that the Dynamic Drainage Jar filtrate was cloudy at the highest level of fiber mechanical treatment in all cases. This indicates that the fiber fines were not completely removed from the furnish here and, therefore, some were lost in the filtrate. This explains the slight decrease in starch retention at the highest level of fiber mechanical treatment. The same phenomenon that occurred with the unclassified pulp occurred in the classified pulp at this point (Figure 10).

FIGURE 9 CLASSIFIED PULP
REFINING TIME VS. STARCH RETENTION

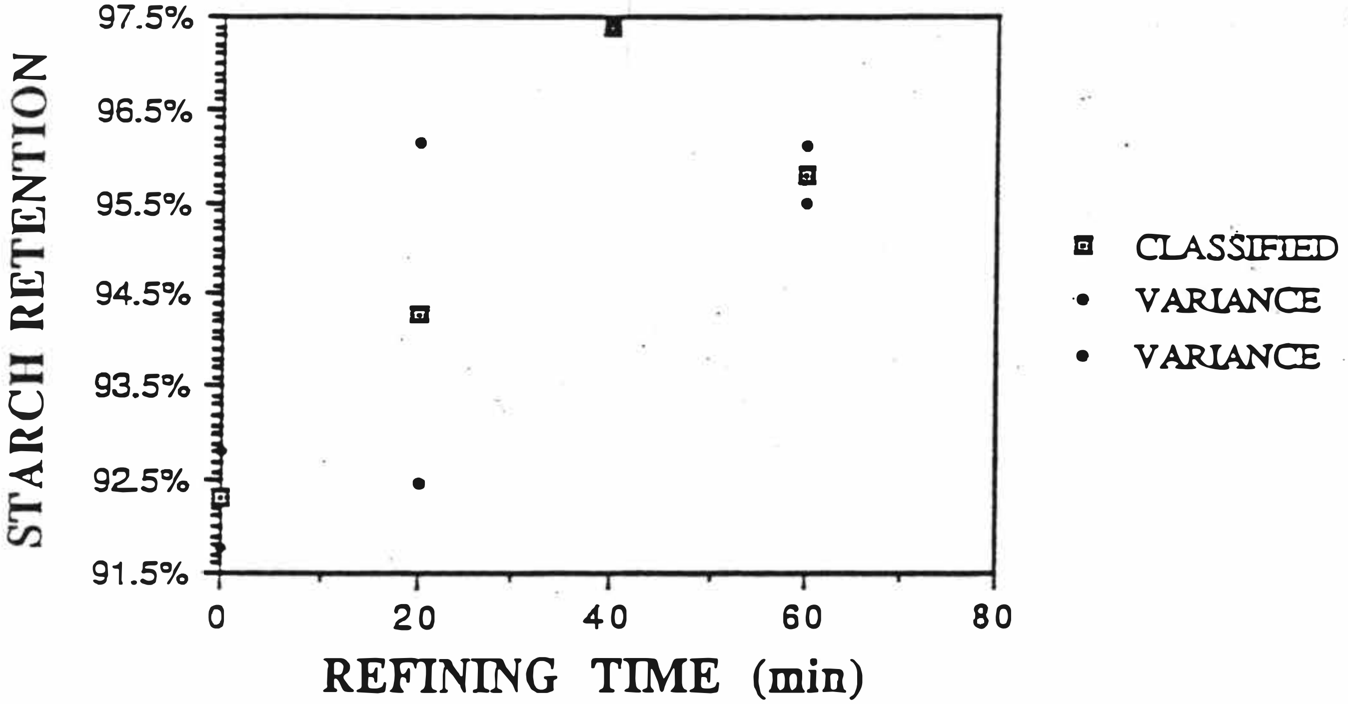
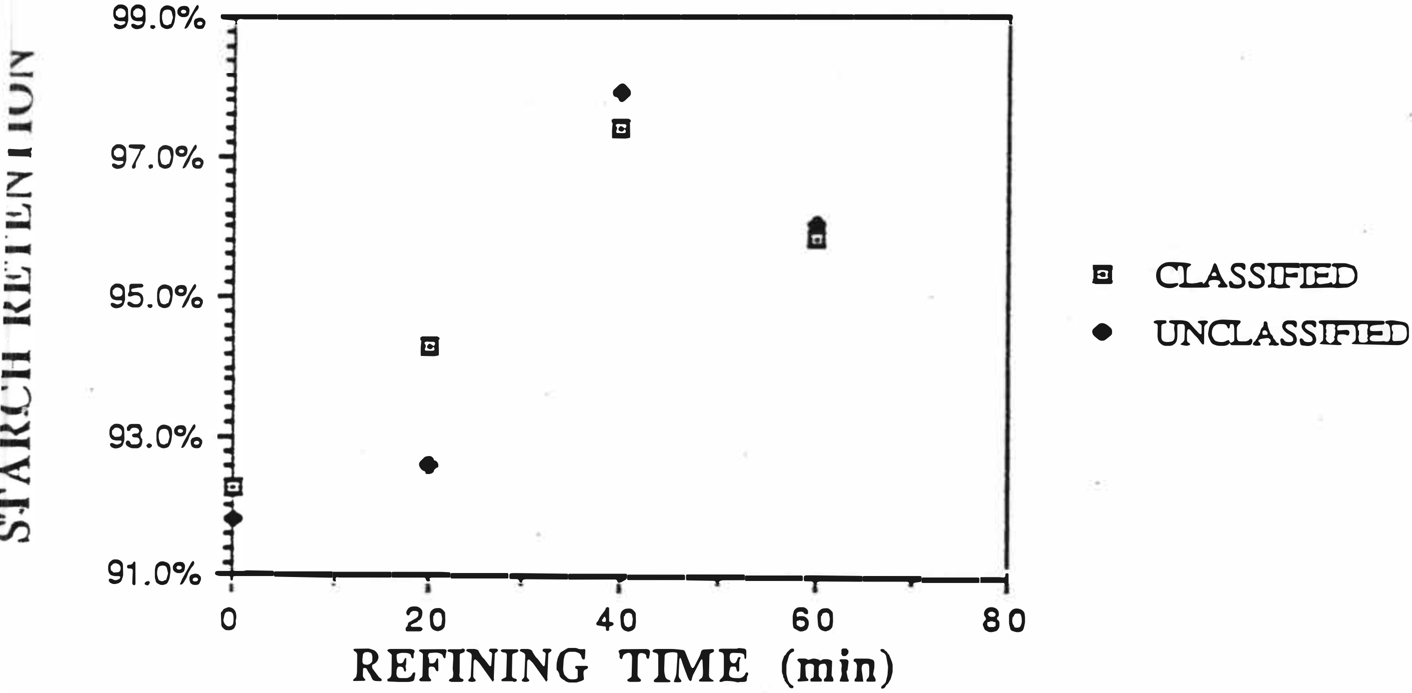


FIGURE 10 CLASSIFIED / UNCLASSIFIED
REFINING TIME VS. STARCH RETENTION



CONCLUSIONS

Based on the literature review, and the data obtained it can be concluded that:

1. Quality and properties of cationic starch vary with starch source and preparation.

2. As cationic groupings progress from primary to quaternary, the charge intensity increases and the sensitivity to pH changes decreases.

3. Cationic starches can increase sheet strength and in some cases can increase fines and filler retention, and also increase drainage rate.

4. Several factors can affect cationic starch retention including:

   - degree of substitution
   - molecular weight
   - rate of application
   - type of furnish
   - retention aid used
   - degree of fiber mechanical treatment

Based on the experimental study of paper, the conclusions may be made:

1. Retention of cationic starch increases as fiber mechanical treatment is increased to a certain point, then decreases as fiber fines are lost.

2. In the absence of fiber fines, fibers will tend to retain more cationic starch the more they are mechanically treated.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Increase starch loading and/or decrease pH in order to obtain a greater variation in retention values.
2. Experiment with different types of fiber furnish.
3. Use classified pulp and vary the amount of fines in the furnish.
4. Determine fiber retention in the Dynamic Drainage Jar.

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APPENDIX I

REAGENTS PREPARATION

$KI-I_2$: This reagent was used as the starch indicator. It was prepared by dissolving 7.5g KI in 10 ml of distilled, deionized water and then dissolving 5g I_2 in this solution and diluting to one liter.

HCl : Several concentrations of HCl were needed to extract the starch from the filtrate. The dilution amounts and approximate normality are as follows:

Dilution	Approximate normality
1 + 0	concentrated
1 + 1	6
1 + 9	1.2
1 + 19	0.6

Cationic starch:

The cationic starch used was pregelatinized, therefore, there was no need to cook it. Moisture content was first determined. 4g o. d. were then mixed in 100 ml cold distilled water for at least 20 minutes. This solution was then diluted by 1% by adding an additional 300 ml distilled water and mixed slowly. Samples were then taken as needed. A starch solution was never used after it was 24 hours old.

APPENDIX II

FURNISH PREPARATION

Moisture content was determined on dry lap pulp samples. 360g o.d. pulp was then slushed with 20 l water for 10 minutes. The slurry was then poured into the Valley beater and the consistency was adjusted to 1.57% with water. The beater was turned on and allowed to run for 5 minutes with no weights. The weights were applied and samples were drawn as previously mentioned.

Some samples were classified in the Clark classifier for at least 10 minutes with a constant flow rate. All samples were filtered in a Buchner funnel. Moisture content was then determined and the stock pads were stored in Ziplock bags.